LINEAR ALPHA-OLEFIN DIMERS

POSSESSING SUBSTANTIAL LINEARITY

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FIELD OF THE INVENTION

5   This invention relates to linear and mono-branched olefin dimers and to methods of making same.

BACKGROUND OF THE INVENTION

Dimerization reactions are widely used industrially and the dimerization of olefins by transition metals has been widely studied. Some reviews or reports of such studies include, for

10   example, a chapter by Yves Chauvin and Hélène Olivier on "Dimerization and Codimerization" in Applied Homogeneous Catalysis with Organometallic Compounds, VCH, New York (Cornils & Herrmann ed. Vol. 1) 258-268 (1996) and a number of articles cited therein.

Many catalysts are known to dimerize olefins, particularly into branched olefins. However, few such catalysts or catalyst systems have shown promising commercial viability due to a variety

15   of limiting factors, including competing side reactions, catalyst cost and activity, lack of selectivity for dimer formation, and severity of the reaction conditions.

The catalysts that are selective for dimer preparation produce mostly vinylidene dimers or di-branched dimers, or they are unselective in product distribution, producing branched, linear, and vinylidene dimers. For example, U.S. Patent No. 4,658,078, issued April 14, 1987 to Slaugh et al.

20   teaches a process for dimerizing alpha olefins to vinylidene olefins. U.S. Patent No. 4,973,788, issued November 27, 1990 to Lin et al. teaches a process for dimerizing vinyl-olefin monomers said to have selectivity of at least 85 percent to form vinylidene olefins but at a slow reaction rate requiring a long reaction time.

W.P. Kretschmer, S. I. Troyanov, A. Meetsma, B. Hessen & J.H. Teuben, "Regioselective

25   Homo- and Codimerization of α-Olefins Catalyzed by Bis(2, 4, 7-trimethylindenyl)yttrium Hydride," 17 Organometallics 284-286 (1998) discusses compounds which are catalysts for various branched dimers including trimers and also for vinylidenes.

H. Heijden, B. Hessen & A.G. Orpen, "A Zwitterionic Zirconocene Alkyl Complex as a Single-Component α-Olefin Dimerization Catalyst," 120 J. Am. Chem. Soc. 1112-1113 (1998)

discusses a zwitterionic zirconocene said to be a single-component catalyst that is highly selective although only moderately active for head-to-tail dimerization of α-olefins.

X. Yang, C. Stern, & T. Marks, "Cationic Zirconocene Olefin Polymerization Catalysts Based on the Organo-Lewis Acid Tris(pentafluorophenyl)borane. A Synthetic, Structural, Solution Dynamic, and Polymerization Catalytic Study," 116 J. Am. Chem. Soc. 10015-10031 (1994) teaches among other things a cationic hydrido complex said to be highly active for the catalytic dimerization of propylene to form a mixture of 2-methyl-1-pentene and 2-methyl-2-pentene.

M. Mitkova, A. Tomov, & K. Kurtev, "A Kinetic Study of Propylene Dimerization by Binuclear Nickel-Ylide Complexes in Presence of Diethylaluminum Chloride as coctalyst," 110 J. Mol. Cat. A.: Chem. 25-32 (1996) discusses propylene dimerization with binuclear nickel-ylide complexes in the presence of diethylaluminum chloride. Various branched-dimer products were obtained.

S. Svejda & M. Brookhart, "Ethylene Oligomerization and Propylene Dimerization Using Cationic (α-Diimine) Nickel(II) Catalysts," 18 Organometallics 65-74 (1999) discusses catalysts prepared from aryl-substituted α-diimine ligands complexed with nickel(II) bromide and activated with aluminum alkyl activators. This article indicates that the active catalysts dimerize propylene generating product mixtures that have roughly equal compositions of n-hexenes and 2-methylpentenes with 2,3-dimethylbutenes as minor products. The catalysts are said to dimerize higher olefins such as 1-butene and 4-methyl-1-pentene very slowly.

Only a few catalysts are known to produce linear alpha-olefin dimers, and these catalysts or catalyst systems generally exhibit low activity and low selectivity. A recent article by B. Ellis, W. Keim and P. Wasserscheid, on "Linear Dimerisation of But-1-ene in Biphasic Mode Using Buffered Chloroaluminate Ionic Liquid Solvents" in Chem. Commun. 337-338 (1999), notes these problems with catalysts for olefin dimerization, but also notes the desirability of obtaining linear olefin dimers, particularly those derived from 1-butene. The article reports some efforts toward improving the activity of known catalysts while retaining dimer selectivity and product linearity.

U.S. Patent No. 5,196,624, issued March 23, 1993 to Threlkel et al. and U.S. Patent No. 5,196,625, also issued March 23, 1993 to Threlkel et al. disclose dimerization processes for

producing linear and mono-branched C_{10} to C_{28} olefins employing a catalyst mixture comprising a nickel(II) compound, a phosphite compound and an alkyl aluminum halide. These processes are said to have high yields.

5   Additional and better catalyst systems or improved dimerization methods for making linear alpha-olefin dimers are still needed, particularly if dimers such as linear 1-butene dimers are to ever be commercially viable.

SUMMARY OF THE INVENTION

The present invention provides linear alpha (α-) olefin dimers that may be produced quickly
10   and efficiently without forming significant non-linear byproducts. The mechanism or process for producing these linear alpha olefin dimers requires a coupling of two olefins per dimer. An initial olefin, such as butene for example, undergoes 1, 2 insertion, and a second olefin, such as butene for example, undergoes 2,1 insertion. A complex results that beta (β-) eliminates to produce the linear dimer, such as 1-butene dimer for example.

15   The coupling is facilitated by a transition metal-based catalyst (or pre-catalyst) that has been activated by an aluminum co-catalyst. The intermediary complex formed is an organo-metallic complex.

The aluminum-based co-catalyst is preferably an alumoxane or a Lewis acid/trialkylaluminum combination such as trialkylaluminum/borane. The transition metal-based
20   catalyst is preferably an iron-based catalyst and most preferably selected from the group having one of the six formulas shown in Figure 2.

The process is preferably carried out under inert atmosphere at a temperature ranging from about zero degrees Centigrade to about eighty degrees Centigrade for these catalysts, although higher temperatures may also be used, depending on the particular catalyst selected. In a batch application,
25   the reaction initially generates heat which may be as high as about eighty degrees Centigrade or higher. This heat of reaction may be controlled by an external water bath or by internal cooling coils. Without cooling, such heat of reaction will generally be sustained until the reaction substrate is depleted. Preferably the temperature is controlled and maintained at a temperature or temperature

range selected for the reaction. In a continuous application, as typical for industrial or commercial applications, a continuous feed of catalyst, co-catalyst and reactant feedstock (i.e., olefins) is supplied and the reaction temperature is maintained within a uniform range.

5   Depending on the metal-catalyst selected and the reaction conditions, the production of linear alpha olefin dimers resulting from the reaction process will range from about thirty percent to about eighty-five percent.

Linear alpha olefin dimers are believed to have many possible diverse uses that have not previously been able to be developed because of prior inefficiencies and difficulties involved in producing such dimers. For example, linear 1-butene dimers will have use in the production of

10   plasticizer alcohols among other things which in turn may be used to make higher quality plasticizing agents for products with less leaching, as particularly needed and useful for example for medical and food packaging applications.

BRIEF DESCRIPTION OF THE DRAWINGS

15   Figure 1 is a diagram showing three pathways--*(i), (ii) and (iii)*--for olefin dimerization, the second *(ii)* of which occurs in the process for making the dimers of this invention and the third (iii) of which results in the formation of byproducts when the dimers of this invention are made. The first pathway *(i)* results in products commonly seen in prior art olefin dimerization processes but does not occur with the present invention.

20   Figure 2 is a drawing of the chemical formulas of six iron-based catalysts or pre-catalysts for making dimers of this invention.

Figure 3 is a plot showing the yield of linear alpha-olefin dimers as a function of reaction temperature.

Figure 4 is a gas chromatograph trace of hydrogenated 1-butene dimers made by the first

25   catalyst of Figure 2.

Figure 5 is an H NMR spectrum of a 1-butene dimer made by the first catalyst of Figure 2.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides linear alpha olefin dimers with methyl-branched olefin dimers as the primary or essentially only by-product. That is, other by-products, such as vinylidenes, tri-substituted olefins and alpha olefins will generally comprise less than about five percent of the reaction product and can occur in so little quantity as to be present in only trace amounts. In an alternative embodiment of the invention, the primary byproduct may be another mono-branched olefin dimer or vinylidene instead or a methyl-branched olefin.

Generally, the mechanism or process for making the linear alpha olefin dimers of this invention requires coupling of two olefins per dimer as shown in the second pathway of Figure 1. The coupling is facilitated by a transition metal catalyst, preferably an iron catalyst, but other metals, such as for example nickel or cobalt may also be used.

A metal hydride resulting from activation of the catalyst or beta-hydrogen elimination is believed to be the active species. This metal hydride gives rise to a primary (1,2) insertion in an alpha olefin to generate a metal-primary alkyl species. To make a linear product, the second olefin exhibits opposite (2,1) regiochemistry of insertion, forming a secondary metal-alkyl bond. Chain transfer leads to a mixture of four linear internal olefin products.

The catalyst should cause the initial 1,2 insertion in the first olefin, as opposed to initial 2,1 insertion, to avoid olefin isomerization and formation of non-linear dimers. Further, the catalyst should preferably prevent or inhibit the formation of vinylidene and branched species. The catalyst should also facilitate rapid beta-hydrogen elimination/abstraction and resultant product release on the dimerization timescale to prevent oligomer or polymer production. Preferably, the catalyst is highly active, converting at least about 10,000 and preferably as much as about 20,000 or more moles of olefin per mole of catalyst per hour. Also, the catalyst should not be reactive toward the dimer product, to avoid product isomerizaton or reincorporation.

A group of catalysts exemplified by the six structures in Figure 2 meet these requirements for a catalyst to make the linear dimers of the invention. Generally, these catalysts are transition metal complexes, preferably tridentate bisimine ligands coordinated to an iron center or a combination of an iron center and aryl rings, either substituted or unsubstituted. Catalysts with less

bulky ligands will yield lower molecular weight products as the molecular weight of the products is dependent to a large degree on the size of the ortho substituents on the 2 and 6 positions of the aryl rings of the ligand.

Referring to Figure 2, complexes 1, 2 and 4 have previously been disclosed as useful catalysts, upon activation, to oligomerize ethylene to linear alpha olefins. Such disclosure, provided in an article by Brooke L. Small and Maurice Brookhart entitled, "Iron-Based Catalysts With Exceptionally High Activities and Selectivities for Oligomerization of Ethylene to Linear α-Olefins," in 120 J. Am. Chem. Soc. 7143-44 (1998), and in PCT patent application no. PCT/US 98/14306 filed July 10, 1998 and published January 21, 1999 as publication no WO99/02472, and especially the description of the synthesis of these catalysts as provided in that PCT patent application, is incorporated herein by reference.

Also referring to Figure 2, complex 6 has been disclosed as an ethylene and propylene polymerization pre-catalyst. These disclosures by Brooke L. Small, Maurice Brookhart, and Alison M.A. Bennett in "Highly Active Iron and Cobalt Catalysts for the Polymerization of Ethylene," 120 J. Am. Chem. Soc. 4049-50 (1998); Brooke L. Small and Maurice Brookhart in "Polymerization of Propylene by a New Generation of Iron Catalysts: Mechanisms of Chain Initiation, Propagation and Termination," 32 Macromolecules 2120-32 (1999); and in PCT Patent Application Serial No. PCT/US/98/00316, filed January 12, 1998, and published July 16, 1998 as publication no. WO9830612, and by Brooke L. Small in his University of North Carolina Doctoral Dissertation, *Diss. Abstr. Int.*, B, 1999, 59(12), and especially the description of the synthesis of this catalyst as provided in said Macromolecules article, are incorporated herein by reference.

For use as catalysts in experiments discussed below, these complexes 1, 2, 3, 4, 5, and 6 of Figure 2 were prepared as disclosed in the references cited above or as discussed in the experimental section below.

The transition metal catalysts, as exemplified by the structures in Figure 2 for making the dimers of this invention, are activated by an aluminum-based co-catalyst. Alumoxanes or Lewis acid/trialkylaluminum combinations, such as trialkylaluminum/borane, are preferred co-catalysts.

Preferred reaction conditions for making the dimers of this invention are an inert atmosphere and room temperature, although a wide range of temperatures may be used. In a batch operation or for batch preparation, addition of the co-catalyst to the metal catalyst quickly increases the heat of the reaction, which will be sustained until the substrate is depleted unless earlier cooled. Cooling

5   may be accomplished with an exterior cooling bath or interior cooling coils. Later, after the initial exothermic reaction has occurred and the reactants cooled, heating may be desired to maintain a desired reaction temperature for dimerization. In a continuous operation or process, as more typically seen in industry or in commercial applications, the catalyst, co-catalyst and olefin feedstock are fed continuously and the reaction temperature is maintained within a selected range.

10   The iron catalysts are active over a wide temperature range, from about zero degrees Centigrade to about eighty degrees Centigrade or higher, although their activity decreases with decreasing temperature. As the catalysts' activities decrease at lower temperatures, their selectivity for forming linear alpha olefin dimer product increases. This higher linear selectivity at lower temperature suggests an increased selectivity for primary (1,2) olefin insertion in the first

15   dimerization step.

Table I shows results of a number of dimerization reactions with the catalysts of Figure 2. Figure 3 plots the data for yield of linear alpha olefin dimers of the invention versus temperature of reaction for reactions with the first catalyst, complex 1, in Figure 2. The temperatures plotted in Figure 3 and listed in Table I reflect the maximum temperatures that the reactions were allowed to

20   reach. In most cases, these temperatures were maintained for about fifteen minutes to about thirty minutes with cooling, until substrate depletion caused a gradual drop in the temperature. External heating was then used to maintain the desired temperature. The plot of Figure 3 shows the linear selectivity for linear product at higher temperatures.

As the catalysts' activities increase at higher temperatures, the lifetimes of the catalysts

25   appear to decrease. As Table I shows (entries 10, 15-17), linear alpha olefin dimer product yields of over seventy percent were achieved with reaction temperatures in the range of about 40 to about 50 degrees Centigrade.

All other conditions being equal, different catalysts will yield different percentages of linear alpha olefin dimers. As shown in Table I, catalysts 1, 2, 3 and 5 of Figure 2 produced mostly linear internal dimers of the invention, while catalyst 4 gave approximately the opposite distribution, with methyl branched internal olefins as the predominant species (as can be seen in entries 6, 8, and 9 in Table I).

Unlike catalysts 1, 2, 3, and 5, catalyst 4 has no alkyl substituents on the aryl rings. Also unlike catalysts 1, 2, 3, and 5, catalyst 4 promoted substantial isomerization in the un-dimerized substrate, thus producing internal olefins. Preferably isomerization does not occur when making the dimers of this invention and generally an advantage of this invention is that remaining or undimerized olefin can be recycled into the process for making the dimers of the invention.

Without wishing to be limited by theory, such isomerization by catalyst 4 may possibly be explained in two ways. First, the non-bulky aryl rings of catalyst 4 may allow the initial insertion to proceed rapidly in comparison to or relative to the second insertion, which causes the rate of beta-hydrogen elimination from the initial insertion to become even more competitive with the second step (olefin addition). Also, since the first step is more likely to proceed with 2, 1 regiochemistry, reversible beta-hydrogen elimination at this stage is believed to result in more isomerized product.

Regardless of the exact reason for increased isomerization by catalyst 4, the increase in methyl-branched dimers from this catalyst shows that the regio regularity of the first olefin insertion step generally decreases with decreasing steric bulk on the ligand. However, the bulkiest of the six catalysts of Figure 2, catalyst 6, showed only a mild increase in selectivity while its activity dropped precipitously over time. Table 1, entry 27, for this catalyst, shows a linear dimer yield of seventy-four percent at forty degrees Centigrade but the conversion rate dropped to less than ten percent after twenty-four hours.

The exact linear dimers produced with the catalysts will vary with the particular feedstocks. Generally, any olefin or neat monomer with accessible double bond in the alpha position may be used as the initial olefin and any alpha olefin or neat monomer may be used as the second olefin. Propylene tends to polymerize rather than result in dimers according to this invention with the catalysts listed in Figure 2. However, the principles of the invention are believed applicable to

propylene with a suitable catalyst. A surprising aspect of this invention is that some catalysts known to be useful for preparing oligomers, particularly propylene (and ethylene) oligomers, as discussed for example in Brooke L. Small's University of North Carolina Doctoral Dissertation, *Diss. Abstr. Int., B.,* 1999, 59 (12), can effectively be used to prepare dimers.

Suitable feedstocks for producing the dimers of this invention are further exemplified by the experiments discussed below:

Experimental

Materials

Anhydrous tetrahydrofuran (THF) and methanol were purchased from Aldrich and used without further purification. Anhydrous cyclohexane was purchased from Aldrich and stored over molecular sieves. Alpha olefins 1-butene, 1-hexene and 1-decene were obtained as commercial grades of Chevron Chemical Company's Gulftene 4, Gulftene 6 and Gulftene 10, respectively. Alpha olefin 1-pentene was purchased from Aldrich. All alpha olefins were dried over molecular sieves. MMAO-3A and MAO-IP were purchases from Akzo Nobel. MAO was obtained from Albemarle Corporation. Tris-(pentafluorophenylborane), 2,6-diacetylpyridine, iron(II)chloride tetrahydrate, and all substituted anilines were purchased from Aldrich and used without further purification.

Synthesis of Ligands for Catalysts 3 and 5 of Figure 2

2,6-bis [1-(5,6,7,8-tetrahydronaphthylimino)ethyl] pyridine (for Catalyst 3)

Chemicals 2,6-Diacetylpyridine (1.0 g, 6.1 mmol) and 1-amino-5,6,7,8-tetrahydronaphthalene (3.6g, 24.5 mmol) were dissolved in a round-bottom flask, to which 50 ml of anhydrous methanol were added. Three drops of glacial acetic acid were added, and the flask was sealed. After stirring the solution for two days, a yellow solid was collected and re-crystallized from methanol to give 760 mg (30%) of the desired ligand for catalyst 3. H NMR (C_6D_6) δ 8.48 (d, 2), 7.30 (t, 1), 7.10 (m, 2), 6.85 (d, 2), 6.56 (d, 2).

2,6-bis[1-(2,4-dimethylphenylimino)ethyl] pyridine (for Catalyst 5)

Chemicals 2,6-Diacetylpyridine (2.0 g, 12.3 mmol) and 2,4-dimethylaniline (8.9 g, 73.7 mmol) were dissolved in a round-bottom flask with a stirring bar, to which 50 ml of anhydrous methanol were added. Three drops of glacial acetic acid were added, and the flask was sealed. After stirring the solution for three days, 3.79 g (84%) of a yellow solid were collected and identified as the desired ligand for catalyst 5. H NMR (CDCl$_3$) δ 8.39 (d,2), 7.85 (t, 1), 7.05 (s, 2), 7.00 (d, 2), 6.60 (d, 2).

Synthesis of Complexes (Catalysts) of Figure 2

The ligand for complex 3--2,6-bis [1-(5,6,7,8- tetrahydronaphthylimino) ethyl] pyridine--and the ligand for complex 5--2,6-bis [1- (2,4 dimethylphenylimino) ethyl] pyridine--were prepared as discussed in the experimental section above. The ligands for catalysts 1, 2, 4, and 6 were prepared as discussed in the references cited above. After preparation, each ligand was separately added in slight excess to iron(II)chloride tetrahydrate in tetrahydrofuran (THF). After precipitation with pentane, the complexes were isolated by filtration for use as catalysts.

Dimerization of 1-hexene and liquid monomers

A two-necked flask with a stirbar was fitted with a reflux condenser on one neck and a thermocouple with the appropriate adapter on the other neck. The apparatus was heated under vacuum, then filled with nitrogen. The condenser was then removed under positive nitrogen flow and the catalyst (or pre-catalyst) (selected from the structures of Figure 2) was added quickly. The flask was back-filled three times with nitrogen and charged with the liquid monomer. Stirring was begun to effectively slurry the sparingly soluble catalyst (or pre-catalyst) in the neat monomer. After several minutes, the aluminum co-catalyst was added via syringe. Many of the reactions were activated at or near room temperature, but the exothermic nature of the reaction often caused the temperature to rise significantly, as reported in Table I.

Table 1. Results for the Dimerization of α-Olefins

Entry	Catalyst	Loading (mg)	Co-catalyst	Al/Fe ratio	α-olefin monomer	Amount (ml)	React. length	React. temp. (°C)	% conv.	Yield (g)	TON	% dimer	% linear internal	% methyl branched
1	1	1.0	MMAO	810	C6	20	3h	25	21	2.8	15,600	92	76	23
2	1	1.0	MMAO	810	C6	20	3h	0	9	1.2	6,700	85	81	18
3	1	5.1	MMAO	560	C4	200	1h	30	22	26.0	42,600	85	71	28
4	2	5.9	MMAO	440	C6	50	1h	30	28	9.4	9,400	87	71	28
5	1	11.7	MMAO	420	C6	200	2h	65	29	39.3	18,700	85	63	36
6[a]	4	10.7	MMAO	340	C6	100	30m	82	58	39.2	23,100	96	27	70
7	1	10.0	MMAO	240	C4	200	1h	40	58	70.6	59,000	83	71	28
8	4	4.3	MMAO	660	C6	100	2h	20	8	5.6	8,200	95	34	65
9	4	6.0	MMAO	480	C6	100	1h	50	44	29.8	31,300	96	29	70
10	1	10.5	MMAO	480	C6	200	5h	40	70	93.9	49,800	83	66	33
11	5	10.5	MMAO	510	C6	200	1h	40	64	86.1	48,400	85	65	34
12	5	6.8	MMAO	390	C6	100	2h	0	33	22.3	19,400	83	80	19
13	5	6.3	MMAO	430	C5, C6[b]	47, 53	1h	40	65	42.8	43,700	85	64	35
14	3	5.5	MMAO	490	C6	100	1h	40	36	24.1	28,600	90	71	28
15	5	26.5	MMAO	80	C6	200	16h	50	76	102.2	22,800	85	63	36
16	1	15.3	MMAO	220	C10	100	2h	45	74	54.7	11,000	85	66	33
17	1	10.0	MMAO	100	C6	100	16h	50	70	46.9	26,100	87	67	32
18	1	10.0	TEA, F15B/25mg	140	C6	200	2h	45	31	43.1	24,000	95	66	33
19	1	10.0	TEA, F15B/25mg	100	C6	200	2h	45	29	39.7	22,100	94	69	30
20	1	10.0	TEA, F15B/25mg	100	C6	200	2h	30	44	59.2	33,000	93	71	28
21	1	10.0	TEA, F15B/25mg	70	C6	200	2h	30	43	59.1	32,900	93	70	29
22	1	50.0	MMAO	250	C20-24	1 kg	26h	50	31	310	~9,500	84	68	31
23	1	10.0	TIBAL, F15B/25mg	120	C6	200	2h	40	36	48.5	27,000	94	67	32
24	1	30.0	MMAO	80	C4	400	1.75h	40	81.5	209	58,100	85	68	31
25	1	30.0	MMAO-IP	105	C4	400	70m	40	57	145	40,500	85	68	31
26	1	100.0	MAO	100	C4	2300	3h	40	42.7	629	52,500	84.6	68.7	31.3
27	6	14.0	MMAO	250	C6	100	24h	40	7.8	5.3	2,200	>95	74	25
28	1	100.0	MMAO	85	C4	2300	3h	40	56.9	785	65,600	83.1	68	31

a) Catalyst 4 causes substantial isomerization of the non-dimerized olefin.

b) Co-dimerization using 1-pentene and 1-hexene in equimolar amounts. GC analysis revealed that equimolar amounts (± 5%) of each monomer were incorporated into the resultant dimers and trimers.

Temperatures were monitored using a thermocouple, and the temperatures listed in Table I represent the maximum temperatures achieved in the reaction. In some cases the exotherm was controlled by a water bath. After reaching the maximum temperature in each reaction, a cooling process was observed, and heating was required to maintain the desired reaction temperature.

5

Dimerization of 1-butene

A Zipperclave reactor was heated under vacuum at 50 degrees Centigrade for several hours. The reactor was cooled to room temperature under nitrogen. The catalyst (or pre-catalyst) (selected from the structures of Figure 2) was then quickly added to the reactor, and the reactor was resealed

10   and placed under vacuum. A dual-chambered glass sample charger was then attached to the injection port of the reactor. From the first chamber a small amount of cyclohexane (internal standard, usually about 20 ml) was added. From the second chamber more cyclohexane (usually about 10 ml) and the aluminum co-catalyst were added. The reactor was then quickly sealed and charged with liquid butene. (Cyclohexane serves as an inactive/inert catalyst carrier.) The reactor was further

15   pressurized with at least 100 psi of nitrogen to keep the butene in the liquid phase. The reaction was stirred rapidly, and the temperature was monitored using a thermocouple.

Product Analysis

The aluminum co-catalysts were removed by pouring the liquid products into a water wash.

20   After removal of the co-catalysts, the products were analyzed by gas chromatography (GC). A Hewlett Packard 6890 Series CG System with an HP-5 50 m column with a 0.2mm inner diameter was used for dimer as well as alpha-olefin characterization. Chrom Perfect™ Version 4 from Justice Laboratory Software was used to analyze the collected data. GC analysis showed clear separation of the linear from the branched species, and hydrogenation of the products confirmed these results.

25   An example of such analysis is shown in Figure 4. C NMR and H NMR were used to confirm the internal olefin content in the products, with only about one percent of vinylidene products present. An example of such an H NMR spectrum is shown in Figure 5.

The conversions and yields were determined by comparing the product to the internal standard integrals, and by assuming equal response factors of the standard and the products. For the hexene dimerization experiments, 1-hexene was the internal standard, and for the butene experiments cyclohexane was used. The approximate density for 1-butene of 0.60 g/ml is included for reference.

5

Hydrogenation of Olefinic Products

The olefinic products in both the dimerization and the alpha-olefin reactions were hydrogenated in a Zipperclave™ reactor at 115 degrees Centigrade and 400 psig hydrogen using HTC Ni 500 catalyst from Crosfield.

10

The foregoing description of the invention is intended to be a description of a preferred embodiment. Various changes in the details of the described product and process can be made without departing from the intended scope of this invention as defined by the appended claims.